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Reports and Papers on the Nature, Uses and Manufacture of Ferro-Chrome and other Ferro-Alloys by S. Monckton Copeman, M.D., F.R.S., Medical Inspector of the Local Government Board, Samuel R. Bennett, M.A., one of H.M. Inspectors of Factories and H. Wilson Hake, Ph.D., F.I.C.



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ARTHUR NEWSHOLME,
Medical Officer,

30th March, 1914.

INTRODUCTORY REMARKS.

BY S. MONCKTON COPEMAN, M.D., F.R.S.

In continuation of the Report on Ferro-Silicon* published as a Parliamentary Paper in 1909, the present report also deals incidentally with some further research work on the properties of this material, but mainly with an investigation on similar lines, of other ferro-alloys, more particularly of ferro-chrome.

In the previous report it was shown that ferro-silicon of certain percentage compositions was prone to disintegration, in presence of moisture especially; and that when this occurred, poisonous gases were given off in such quantity as to bring about fatal results in human beings subjected to such emanations.

About a year later evidence was obtained, for the first time, that another ferro-alloy which is used in the steel industry in greater quantity than ferro-silicon—ferro-chrome—might, in like manner, undergo disintegration with concomitant evolution of poisonous gases. Further, as regards certain other ferro-alloys, also, evidence has been forthcoming, that under special conditions they may exhibit similar characteristics.

In June, 1910, I received information to the effect that of a consignment of several tons of ferro-chrome received from France, by a large Sheffield firm, samples had been found to evolve "acetylene-smelling gas, more strongly than the worst 50 per cent. ferro-silicon." The samples were also found to fall to powder very readily on exposure to air and moisture; and paper impregnated with silver nitrate assumed an intense black colour almost immediately on exposure to the fumes given off from this material, while lead acetate paper was unaffected, thus indicating the evolution of phosphoretted hydrogen gas in large quantity.

* Supplement to the 38th Annual Report of the Medical Officer of the Local Government Board, 1908-09 (Cd. 4958-1909).

This particular consignment of ferro-chrome, manufactured, as I subsequently learnt, by one of the largest makers of ferro-alloys in the south of France, was found to contain an abnormally high percentage of silicon, and to this fact, apparently, the consignees were inclined to attribute the peculiar ease with which the material crumbled "unlike ordinary ferro-chrome which is almost as hard as cast-iron."

As an indication of previous absence of information of the possibility of spontaneous disintegration in the case of ferro-chrome, it may be mentioned that in a letter dated 15th February, 1909, the Board of Trade, in reply to enquiries by Messrs. Wilson, Sons & Co., Ltd., of Hull, stated that "they were advised that no danger is likely to arise from the carriage of the ordinary commercial varieties of this substance (ferro-chrome), on board ship." Messrs. Wilsons' enquiries were made in consequence of a report (11th February, 1909) received by them from an analyst, Mr. J. Evans, F.I.C., of Hull; the last two paragraphs of this report being worded as follows:—"We therefore strongly advise that the same precautions be taken with this substance (ferro-chrome) as were recommended in the case of ferro-silicon, as we see no reason why certain samples of ferro-chrome should not be equally dangerous. The same remarks will apply to other ferro-compounds, which are manufactured in the electric furnace."

In view of the information received by me, and after consultation with representatives of the Home Office and of the Board of Trade, it was decided that under the circumstances it was desirable with the concurrence of the Local Government Board that further investigation of the question should be undertaken, and that, as a preliminary step, samples of ferro-chrome, especially from consignments recently imported, should be obtained and investigated.

To this end I received instructions from the Board to arrange with Dr. Wilson Hake, who had been associated with me in the Ferro-Silicon enquiry, to undertake the chemical examination of such samples of ferro-chrome as might be supplied to him in connection with the enquiry. As regards the actual collection of material for this purpose, Sir Arthur Whitelegge, Chief Inspector of Factories at the Home Office, kindly arranged that the services of Mr. S. R. Bennett, one of H.M. Inspectors of Factories at Sheffield, who had assisted me in my Ferro-Silicon enquiry, should be placed at the service of the Board to such extent as might prove necessary for this purpose.

In due course a preliminary series of samples of ferro-chrome were received from Mr. Bennett which were sent on to Dr. Hake for investigation. Certain of these he found had already spontaneously disintegrated, and yielded a marked qualitative reaction for phosphoretted hydrogen. But, from the data supplied by Mr. Bennett with the specimens, it was apparent that most of the material from which his samples were taken had been "in stock" at the various works in Sheffield at which he obtained them, for some time previously. In view of this circumstance Dr. Hake and I came to the conclusion that a further investigation of samples as freshly manufactured as it might prove possible to obtain,

accompanied in each instance by full and complete data as to source, composition (manufacturers' and works' analyses), date of manufacture, etc., would be desirable, in order to render possible more definite decision as to potentiality of danger in the transport storage and use of this material.

In the course of my previous investigation of possible danger under similar circumstances, from ferro-silicon, I had made careful enquiry in various directions as to the possibility of ferro-chrome of any particular percentage composition, under any circumstances exhibiting the liability to disintegration, which by the universal consent of those having occasion to deal with ferro-silicon is characteristic of certain percentage grades of this latter substance when exposed to the action of air and moisture. At this period, however, manufacturers and users of ferro-chrome, as also many agents and works' chemists to whom I applied, were unanimously of opinion that ferro-chrome differed entirely from ferro-silicon in that it was invariably of a hard and compact nature somewhat resembling pig-iron; and this, whatever the particular percentage composition might happen to be.

When therefore, a year or so later, it came to my knowledge that certain consignments of this alloy had been found capable of disintegration in similar fashion to ferro-silicon of about 50 per cent. silicon content, the comminution in the instance that first came under notice being so complete that the workmen spoke of the resulting powder as "flour," it seemed fairly obvious that one or more of the firms manufacturing this alloy must in some way have departed from the methods originally employed, seeing that the alteration in physical characteristics did not coincide with the marketing of percentage grades other than those previously supplied for commercial purposes, at any rate, so far as the chromium content was concerned.

In this connection I may refer to certain suggestions put forward in my report on ferro-silicon (page 109) bearing on the reason for the specially undesirable qualities—tendency to spontaneous disintegration and evolution of poisonous gases—of the particular grade of ferro-silicon containing, as shown by chemical examination, about 50 per cent. of silicon. I there state that in the course of an interview with Dr. Heroult, the managing director of the Société Electro-métallurgique Française, he expressed the opinion that the particular characteristics of the grade referred to above would be found to be related to the amount of *aluminium* present in the alloy. He was unable, however, so far as I could gather, to advance any definite reasons for the opinion he had formed. But I was specially interested when, later on, in the course of correspondence, Mr. Bennett, who, at the time was engaged on work in connection with my general investigation, made the same suggestion, basing it on the fact that he had noticed that the amount of aluminium in samples of the consignment of ferro-silicon which had caused a series of explosions at Liverpool in 1904 was unusually high as shown by chemical analyses made at the time.

Mr. Bennett suggested that as the heat of formation of Al_2O_3 is very great—392,000 calories approximately—the presence of a

large percentage of aluminium in ferro-silicon might be indicative of very high temperature reactions having taken place in the electric furnace, and that these reactions are favourable to the formation of compounds which readily break up into poisonous and explosive gases.

Further evidence, in this case of an experimental nature, as to the possible influence exerted by the presence of aluminium in rendering ferro-silicon liable to disintegrate spontaneously reached me, in a letter from Mr. Olsen, of Christiania, the representative of a firm engaged in the manufacture of this material. He informed me that he had carried out a number of experiments with the object of determining the reason why certain samples of ferro-silicon should disintegrate, while others do not. As the outcome of these experiments he found, as he informed me, that aluminium has "a great effect" in this connection. For if, in the course of manufacture, aluminium is purposely added, so as to raise the aluminium content of the final product, he found that "at certain percentages," which, however, he did not explicitly indicate, "the ferro-silicon can scarcely be kept for a few minutes without falling to pieces." Mr. Olsen stated, in conclusion, that he was still continuing his experiments; but as to the results that he may have obtained from the further investigation contemplated by him, up to the present, no further information has been received.

The supposition as to the important physico-chemical rôle apparently played by the presence of aluminium in ferro-silicon was further strengthened by the outcome of certain experiments reported to me as having been carried out at Sheffield. Two samples of ferro-silicon were manufactured in a small electric furnace, care being taken to insure that the materials employed should be as free from impurities as possible. Into one of the samples, however, pure aluminium was purposely introduced in sufficient quantity to constitute two per cent. of the finished alloy. This latter sample subsequently proved to be specially liable to disintegration, giving off at the same time large quantities of phosphoretted hydrogen gas; while the other sample, free from aluminium, did not disintegrate, although of practically the same percentage composition, and exposed to similar conditions in all respects.

Shortly after the fact that certain consignments of ferro-chrome had been found to disintegrate spontaneously, with evolution of strongly smelling fumes, had come to my knowledge, I also learned that in one continental manufactory, at any rate, a new method, known as the Thermite Process, had recently been brought into operation in connection with the commercial production of ferro-chrome. As this process depends for its success on the enormous amount of heat produced by the combustion of powdered metallic aluminium, the possibility at once presented itself that manufacture of ferro-chrome by this process, which would be likely to result in the alloy produced containing aluminium in perhaps considerable quantity, and the potentiality for disintegration of the alloy might not improbably be found to bear the mutual relationship of cause and effect.

During the course of a visit to Sheffield, which afforded opportunity for consultation with officials of several of the large manufacturing firms there, who had so courteously put at my disposal their expert knowledge in connection with my previous investigation as to possible danger during the transport and storage of ferro-silicon, Mr. Brearley, chemist to Messrs. Firth & Son, Ltd., most kindly undertook the examination of certain samples of ferro-chrome, with special reference to their aluminium content.

So far as I was able to learn, the first consignment of ferro-chrome received in Sheffield which is known to have exhibited the physical property of disintegration, coupled with abundant evolution of acetylene-smelling gas, was received early in 1910 from France, presumably *via* Havre and Hull. It was invoiced (April 19th, 1910) at 66·2 per cent. chromium, but three separate works' analyses gave :—

Percentage Composition.

Chromium	...	...	64·7	—	64·9
Silicon	...	...	5·0	4·68	3·4
Carbon	...	...	8·15	—	—
Iron	...	...	By difference.		

(The absence of figures denotes that no estimation of the particular constituent was made.)

It may here be mentioned that two kinds of ferro-chrome are utilized in various manufacturing processes, which are known respectively as low and high carbon ferro-chromes. The amount of silicon in high carbon ferro-chrome, of which the consignment in question is a sample, also varies greatly, ranging from less than 0·5 per cent. to nearly 4 per cent.; the high silicon variety being used for the hardening of armour plates. It will be seen from the works' analyses given above that this particular consignment contained an abnormally high percentage of silicon, and somewhat naturally therefore the question was mooted locally as to whether its unusual characteristics, *quâ* disintegration and evolution of gas, might not be in some way related to the abnormal silicon content. In this particular instance it had not apparently occurred to any of the works' chemists concerned to estimate the amount of aluminium present.

In December of this same year (1910), however, Mr. Brearley, in accordance with his promise, sent me a series of very complete analyses of samples of ferro-chrome, selected from a consignment of 44 casks received from an important manufactory in the south of France. In these analyses special attention was paid to the amount both of aluminium and silicon in each instance. The amount of silicon, although high, varied in the different samples, within comparatively narrow limits; whereas with regard to the aluminium content, as indicated by the analytical results, the facts are quite otherwise. The report states that in some of the casks the alloy consisted of good clean lumps which varied somewhat in

hardness, these being referred to in the subsequent analyses as "hard" and "soft." In other casks the larger pieces were buried in very fine powder; and there could be distinguished two kinds of alloy, differing in physical properties from anything that had been previously met with in the examination of samples of ferro-chrome. These were:—

- (1) Friable lumps which broke to pieces when dropped on to the stone floor. In the subsequent analyses this is referred to as "coarse" material.
- (2) Friable pieces having the appearance of matted moss, which broke in the hand on attempting to remove from the mass, and which could be rubbed to powder between the fingers. This is alluded to in the following analyses as "fine."

The contents of all the casks were sieved, and about two tons of very fine material thus obtained. The composition of the four kinds of material already mentioned is as follows:—

—	C.	Si.	Mn.	S.	P.	Cr.	Al.	Fe.
Hard	8·20	6·06	·55	·014	·014	67·56	None	18·37
Soft	8·75	5·55	·41	·021	·008	68·19	None	17·92
Coarse	7·11	7·66	·13	·007	·017	61·84	2·01	21·32
Fine	6·95	6·91	·32	·005	·027	58·80	7·41	19·50

Samples of the various classes enumerated above were sent to me by Mr. Brearley, and in due course handed over to Dr. Hake for further examination.

The contrast between entire absence of aluminium in the first two of these samples, and the presence of so large an amount of this metal in the last two, more especially in the "fine" sample, is decidedly remarkable.

As the result of inquiry of several of the larger steel manufacturing firms at Sheffield, it is obvious that even at the present time it is not by any means a usual experience to meet with evidence of disintegration in consignments of ferro-chrome. For instance, a letter was received from Messrs. Vickers, Sons, & Maxim, Ltd. (now "Vickers, Ltd.") in which the following statement occurs:— "Our chemist has examined samples from our present stock of ferro-chrome, but cannot find any aluminium in it, neither has he at any time noticed a tendency to disintegration."

But the very fact that it is apparently a somewhat rare occurrence for ferro-chrome to exhibit this peculiar physical property makes it all the more important that the possibility of such an event, accompanied, as is likely to be the case, with the evolution of large quantities of gas (phosphoretted hydrogen) of highly poisonous nature, should be generally realised. Otherwise, as in connection with the use of ferro-silicon, lives may be sacrificed through ignorance on the part of those brought in contact with this material, of the necessity for observance of due measures of precaution.

Thus far, however, no evidence has been obtained as to accidents, fatal or otherwise, having arisen in connection with evolution of poisonous gases from ferro-alloys other than ferro-silicon.

But ferro-chrome is not the only ferro-alloy in addition to ferro-silicon which has, on occasion, been found to undergo disintegration. Thus Mr. Harbord informed me that after an extensive fire at premises where a large consignment of blast-furnace ferro-manganese happened to be stored, he had found that much of this material had become oxidised and disintegrated as the result of contact with the quantities of water necessarily used for the extinction of the conflagration.

Careful examination of the literature of the subject has revealed two references, by R. Dubois* and O. Sunnersbach† respectively, to the occurrence of disintegration in the case of ferro-manganese, one of these dating back as far as 1902. And it is of special interest to note that, in each instance, an 80 per cent. alloy was in question. Dubois says of the sample examined by him that, having been kept in the open for a couple of months, it so completely fell into powder that the mass of material was reduced to one-half its previous bulk. These experiences with 80 per cent. ferro-manganese, viewed in conjunction with Mr. Harbord's observation on a sample of blast-furnace product, renders it not improbable that, as in the case of ferro-silicon, there may be at least two points corresponding to certain fairly definite percentages of alloy, at or about which, under favouring circumstances, disintegration may be specially liable to occur.

In view of the importance of obtaining further information as to the chemical and physical constitution of various ferro-alloys, of which, commercially, ferro-silicon and ferro-chrome are the more important, I received instructions from the Board to arrange with Dr. Wilson Hake to carry out a further series of investigations, with special reference to the aluminium content of the various grades of these alloys.

Numerous samples of ferro-chrome were obtained from various steel works and agents, especially in Sheffield, all of which were of foreign manufacture. At Sheffield also was obtained a sample of 50 per cent. ferro-silicon which, as regards capacity for disintegration, and evolution of phosphoretted hydrogen gas, was the worst that has been encountered in the course of our investigations. This particular consignment had been refused by the purchasing firm, and was about to be sent back to the manufacturer abroad; but happening to be in Sheffield at the time, and information having reached me as to the circumstances, a specimen (No. 19 in Dr. Hake's Table) was promptly secured.

A few samples of ferro-manganese of foreign origin were also obtained.

Through the courtesy of the Newcastle Alloy Company, Limited, whose recently installed works I was afforded opportunity of inspecting in company with Mr. Peile, the Chairman, samples

* R. Dubois. Bulletin de l'Association Belge des Chémistes. 1902. Vol. xv., p. 221.

† O. Sunnersbach. Stahl und Eisen. 1905. Vol. xxv., pp. 617, 618.

of their electrically-produced ferro-silicon of 75, 50 and 25 per cent. grades (nominal) were received, and subsequently submitted to Dr. Hake whose report on the examination of all the samples received by him is published herewith. The general lines on which his investigations were carried out, and the probable interpretation of the results obtained, have been the subject of frequent conference between us during the progress of the work.

Conclusions.

The results of Dr. Hake's investigations may be briefly summarized as follows :—

Ferro-chromes.—There would seem to be no doubt that an excess of aluminium in these alloys is coincident with a tendency to spontaneous disintegration, accompanied by evolution of phosphoretted hydrogen.

Ferro-silicons.—Although in most instances the aluminium found corresponds with the amount present in the coal used in the furnace charge, one sample which exhibited definite disintegration and evolution of poisonous gases was found to contain an exceptional amount of this metal. Arguing from analogy to ferro-chromes, however, it seems not unlikely that owing to reduction of aluminium in the electric furnace, and subsequent oxidation, the amount found in the final product may not appear excessive, although prior to such oxidation of the aluminium having taken place, the presence of the metal may have been responsible for a considerable reduction of calcium phosphate to phosphide.

Silico-Manganese.—Only two samples of this alloy were available for examination. Both were of a somewhat suspicious character, as regards tendency to disintegration and evolution of poisonous impurities, a fact suggestive of possible danger in connection with the transport, storage, and use of this material.

Ferro-Manganese.—Two samples examined showed only traces of impurities. As, however, cases of spontaneous disintegration of this alloy (to which I have directed attention earlier in this report) are known to have occurred, further knowledge on this point is needed.

Electro-Manganese.—The one sample examined contained 95 per cent. of metallic manganese and was free from impurities. But attention must be directed to the fact (not apparently previously recorded) that this product evolves hydrogen copiously when brought into contact with water even at ordinary temperatures, but especially if the latter be warm. In the event of hydrogen being thus generated during transport, especially on board ship, such an occurrence would be likely to give rise to considerable danger owing to the highly explosive nature of a mixture of this gas with air.

S. MONCKTON COPEMAN.

THE USE OF FERRO-CHROME IN THE MANUFACTURE OF STEEL.

By S. R. BENNETT, M.A.

The researches hitherto conducted on ferro-chrome alloys may be summarised under the heads—

- (1) History; (2) Manufacture; (3) Constitution and Properties; (4) Functions in Steel Manufacture.

(1) *History.*

The properties of alloys of iron and chromium have been made the subject of investigation, to some extent, for many years past. M. Brustlein in his remarkable memoir, presented to the International Congress of Mines and Metallurgy in 1889, quotes Berthier as mentioning chrome steels in a work published in 1820, in which, referring to the method of producing ferro-chrome, he predicts that it will be used for cast steel. Later, Boussingault took up this question, and noted the presence of 3 per cent. to 4 per cent. Cr. in steels made in 1867, near Medellin, Antiochia, Central America. However, it was in the United States of America that industrial chrome-steels were first produced on a somewhat large scale. M. Rolland, engineer to the Corps of Mines, published in 1878, a report on the manufacture of high-resistance chrome-steels at Brooklyn. Earlier still, in 1875, M. Brustlein instituted a series of experiments at the steel works of H. Holtzer & Cie., at Unieux, which inaugurated a new branch of the metallurgical industry in Europe. Further description naturally falls under the head of Manufacture.

(2) *Manufacture.*

Ferro-chrome has been made by four different processes, involving the use of:—(a) coke-fired crucible furnaces; (b) blast-furnaces; (c) electric furnaces; and (d) the Thermite or Goldschmidt process.

Ferro-chrome was, in the first instance, made in crucibles. Chrome iron-ore, previously powdered, was mixed with 6 per cent. to 8 per cent. of carbon in the form of charcoal or anthracite. This mixture was melted in graphite or magnesia crucibles by aid of such fluxes as alkaline fluorides mixed with lime, borax mixed with carbonates, bottle-glass, etc., and raised to a high temperature. The ores used at Unieux contained 27 per cent. chromium and 14 per cent. iron. At Brooklyn, ores containing 21 per cent. to 46 per cent. chromium were used. Poor ferro-chromes are still made in crucibles to a small extent.

Later these alloys were produced in blast-furnaces, in the form of chrome pig-iron. The limit reached in chromium content is usually 30 per cent. to 40 per cent., although some containing up to 60 per cent. have been made. The process differs but slightly from that by which ordinary pig-iron or silicon pig-iron is produced. A very large consumption of fuel is required—about three tons of coke per ton of 40 per cent. chromium alloy. Also the ferro-chromium is usually high in combined carbon, and is apt to contain sulphur unless special precautions are taken.

Most rich ferro-chromes are made in the electric furnace by direct reduction of chrome iron-ore with carbon, coke or charcoal, the heat of fusion being furnished by the electric current. As stated above, the composition of this ore varies greatly according to the source of supply. For that used in the electric furnace an average composition would be

$$\begin{aligned}\text{Cr}_2\text{O}_3 &= 50 \text{ per cent.} \\ \text{FeO} &= 25 \text{ ,,} \\ \text{Al}_2\text{O}_3 &= 10 \text{ ,,}\end{aligned}$$

Lime, Silica, Magnesia, &c., variable.

It is found in Scotland, France, Eastern Europe, Asia Minor and New Caledonia; deposits occur also in the United States and New South Wales.

Pioneer work with the electric furnace was carried out by H. Moissan, who, in his book "Le Four Electrique," thus describes the formation of ferro-chrome:—Powder the mineral (chrome iron-ore) finely, add to it an amount of carbon corresponding to the oxygen and heat in the electric furnace. Using a mass of about four lbs. and current of 1,000 amperes at 60 volts, there was obtained in a few minutes a fused mass of ferro-chrome of composition as follows:—

$$\text{Cr} = 60.9, \text{Fe} = 31.6, \text{C} = 6.1, \text{Si} = 1.1 \text{ per cent.}$$

$$\text{Total } 99.7 \text{ per cent.}$$

To refine the alloy thus formed, it may be fused in a bath of molten lime in the electric furnace. A first fusion reduces the carbon to about 4 per cent., and the second to about 0.1 per cent.

For example, a ferro-chrome composed of:—

$$\text{Cr} = 61.81, \text{Fe} = 30.02, \text{Total C} = 7.53, \text{slag } 0.33$$

gave when fused in a bath of molten lime a metallic regulus containing 4.2 per cent. C; while on repeating the operation—care being taken not to continue the process too long—the result was

$$\text{Cr} = 64.00, \text{Fe} = 35.12, \text{C} = 0.7, \text{slag } 0.22.$$

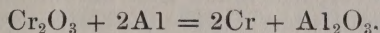
The electric furnace, however, was not used for production commercially until about 1892, some time before ferro-silicon was so made. The arc is produced between electrodes usually outside the bath, to prevent re-carburization. The usual mixture for the charge is

chrome iron-ore (50 per cent. Cr_2O_3)	...	100 parts,
coke or anthracite		21 ,,

with which a ferro-chrome containing 60 per cent. to 64 per cent. Cr, and about 9 per cent. carbon will be produced. To refine this alloy it is crushed and placed in a bed of the following composition, viz.:—crushed ore 14 parts, lime 2 parts, for every 100 parts of alloy to be refined. By repeating the operation several times, 4 per cent. carbon ferro-chrome is obtained, but to attain this, furnaces containing no trace of carbon must be used.

To obtain ferro-chromes with less than 4 per cent. carbon, M. Guillet says, "methods which are kept absolutely secret must be employed. To such a point is secrecy preserved, that at the Giffre factories the furnaces in which these are made are surrounded by high walls."

The Goldschmidt or Thermite process is one of direct reduction, depending upon the powerful affinity of aluminium for oxygen, whereby it is able to combine with the oxygen of chromic oxide, leaving the chromium in a free state. The re-action may be represented thus—



The heat produced is so great that methods have to be adopted of controlling the re-action. The usual procedure is as follows:—molecular parts, 15.28 Cr_2O_3 and 5.42 Al, are mixed in a well-dried crucible lined with magnesia calcined at a not too high temperature. On the top of the mixture is placed a small heap of an ignition powder made by mixing powdered aluminium with an easily reducible oxide such as barium or sodium oxide; and into this heap is inserted a short piece of magnesium wire or cordite. The ignition of the magnesium wire, or the cordite, is sufficient to start the re-action in the ignition powder, which is then communicated to the mixture in the crucible. When the re-action is fairly started, the remainder of the chromic oxide and iron mixed with the requisite amount of aluminium are slowly charged into the crucible. The reduced alloy settles to the bottom of the crucible, under a layer of slag consisting of fused alumina. This process has been used at Essen for the manufacture of ferro-alloys.

(3) *Constitution and Properties.*

The series of ferro-chromes are, on the whole, more solid and of closer texture than ferro-silicons. Large cavities are seldom met with, except in impure specimens containing excess of silicon and carbon sufficient almost to constitute silico-ferro-chromes. M. Brustlein, who studied the properties of ferro-chrome, states that the aspect of the fracture varies much more with the carbon content than with the proportion of chromium. When the alloys are charged strongly with carbon and silicon, or with carbon alone, they present an acicular Martensitic structure. Their hardness and brittleness increase with the amount of these elements. For alloys low in carbon (2 per cent. to 3 per cent.) and in chromium (16 per cent.) he observed a fracture containing rectangular cleavages.

H. von Jüptner has found that these acicular crystals are attacked with difficulty by acids, and consist of iron chromium carbides, the composition varying apparently with the percentage of chromium present. The carbides Cr_2FeC_2 and $\text{Cr}_2\text{Fe}_7\text{C}_3$ have been detected in 50 per cent. ferro-chrome and in 30 per cent. ferro-chrome respectively. That is, either these or their

polymers have been isolated. MM. A. Carnot and Goutal examined the following ferro-chromes :—

I. Fe = 32.6, Cr = 57.6, C = 9.9,

II. Fe = 32.2, Cr = 59.1, C = 9.1,

by treatment with HCl, and found $\text{Fe}_3\text{Cr}_9\text{C}_7$, which may be constituted as $\text{Fe}_3\text{C} : 3\text{Cr}_3\text{C}_2$. Fe_3C is the constituent cementite found in steels, and Cr_3C_2 carbide was obtained by Moissan in his earlier experiments. But chromium is said to exist in another form in iron also, viz., distributed or dissolved in the main mass of the metal, and therefore readily soluble when treated with acids. Le Chatelier, however, has found that chromium, unlike tungsten or molybdenum, modifies but slightly the electric resistance of steels, and concludes therefore that the chromium does not exist in a dissolved form in the metal.

Chrome steels contain a double carbide whose composition seems also to vary with the chromium content ; since, as is well known, picrate of soda colours this carbide less easily the more chromium the material contains. If a rich chrome steel is treated with aqua regia, the carbide, when it is rich in chromium, is unattacked. These crystals of carbide are sometimes well developed, and are often surrounded by eutectic. In ferro-chromes containing about 65 per cent. Cr and 5 per cent. C, it is found to be a difficult matter to make the texture appear with aqua regia ; if for the same chromium content the carbide be increased it cannot be attacked, and the mass appears as if homogeneous. Sometimes the carbide is found in layers surrounded with pearlite, which is not susceptible of being coloured with picrate. For very high chromium content (99 per cent.) immense polyhedra of chromium are obtained, surrounded by small quantities of carbide which cannot be coloured. Whereas fine-grained cast chromium with 1.5 per cent. to 3 per cent. carbon can only be worked and polished with a diamond wheel, refined chromium (density 6.4 to 6.8), free from carbon, may be filed with ease, and takes a brilliant polish like that of iron, but somewhat whiter. This latter substance is very difficult to obtain, as the chromium oxidises quickly.

The only systematic investigation of these alloys is apparently that of Trietsche and Tammann (*Zeit Anorg. Chem.*, 1907, 55, 402). The alloys were investigated by Thermal analyses, being fused in magnesia tubes at 1,700° Centigrade before the cooling curve was taken. The curve of commencement of solidification is irregular, showing minima at about 15 per cent. and 40 per cent. Cr respectively 1,440° Centigrade, and maxima at 30 per cent. Cr and 90 per cent. Cr (1,450° Centigrade and 1,610° Centigrade). There is another irregular curve, presumably the solidus, the temperature on which falls at first with increase in the amount of iron, and then rises to the melting point of the latter metal. There is also a halting place and eutectic at about 1,260° Centigrade between 30 per cent. and 60 per cent. Cr. These facts led the authors to suggest that this system is one in which a compound of Fe and Cr forms with difficulty, and equilibrium is not attained ; hence the behaviour is as in a ternary system of Fe, Cr, and a third body X

(similar to Fe-Mo). This body (unlike the Fe-Mo compound) is completely miscible in the solid state with its components. The observations are represented on a projected space diagram, on which the two surfaces representing these series will not extend into the binary systems CrX, FeX. The break on the cooling curve at 1,260° Centigrade represents a eutectoid in which the two series of mixed crystals and the eutectic crystallise together. The microscopic examination bears out these conclusions. All the alloys from 10 per cent. to 90 per cent. Cr consist of two structural elements, the one which separates primarily being softer and more readily attacked by acids than the secondary.

Alloys were also prepared by the Goldschmidt or Thermite process and were found to be homogeneous, consisting of polyhedral crystals. On heating these alloys at 1,700° Centigrade for some time, they regain the structure of those prepared at that temperature, so that equilibrium is attained fairly rapidly at high temperatures. All the alloys up to 80 per cent. are magnetic.

(4) *Functions of Ferro-chrome in Steel Manufacture.*

Chromium as a constituent of steel confers important physical properties. For steels low in carbon, those containing less than 7 per cent. Cr are pearlitic in structure; from 7 per cent. to 15 per cent. Cr Martensite or Troostite is the main structure; above 15 per cent. Cr double carbides appear as small particles, white and very hard. As the proportion of carbon content increases, so these changes of structure occur with smaller percentages of chromium. Thus with 0.8 per cent. C the passage to Martensitic steel takes place at about 5 per cent. Cr. Of these steels the pearlitic alone are of any industrial value. Those containing the double carbide are too brittle and too hard, offering but medium resistance to shock. The pearlitic steels are hard, the hardness increasing rapidly with the proportion of chromium; they exhibit high resistance to rupture, and high elastic limit, giving elongation and reduced section equal to some ordinary steels, but are generally more brittle. Like all pearlitic steels, hardening produces Martensite, but of a very hard character.

Such chrome steels are mainly used for armour plate, armour piercing projectiles, some high-speed steels, steel for stamps and crushers, also for files, tyres, springs, &c. But it is owing to the important controlling influence of other metals, such as nickel, tungsten, vanadium, &c., that most of them are made useful in the highest degree.

Chrome steels are prepared either in the Martin furnace, converter or crucible. The most convenient method of conveying the chromium into the bath is by means of a suitable ferro-chrome alloy. The alloy is added to the bath before tapping, or may be melted separately and run into the converter or ladle. Unlike ferro-silicon, none goes into the slag, and it exerts no de-oxidising influence on the occluded gases in the molten metal. As to the most suitable ferro-chrome to be employed, this depends on the

composition required for the final product in carbon and chromium. The cheaper ferro-chromes may contain nearly 10 per cent. of carbon, and consequently cannot be used when low carbon steels are required, except under special conditions. High carbon ferro-chromes (*i.e.*, over 6 per cent. carbon) are used mainly in projectiles (2 to 4 per cent. Cr.), and for stamps, crushers (0·5 to 1 per cent. Cr.), &c. Both high and low carbon ferro-chromes are used in armour plate (about 2 per cent. Cr.) and in special steels; mostly high carbon for the former, but low carbon for the latter. For high-speed steels, low carbon ferro-chrome is almost invariably used, and is added in the crucible. Chrome steel for files contains 0·5 per cent. to 0·7 per cent. carbon and 2 to 3 per cent. chromium, the higher percentages giving extremely hard tools.

S. R. BENNETT.

REPORT ON THE EXAMINATION OF VARIOUS FERRO-ALLOYS WITH SPECIAL REFERENCE TO THEIR ALUMINIUM CONTENT AND ITS POSSIBLE BEARING ON THEIR STABILITY AND SAFETY.

By H. WILSON HAKE, Ph.D., F.I.C., F.C.S.

A Supplement to the 38th Annual Report of the Medical Officer of the Local Government Board, 1908-9 (Cd. 4958, 1909), dealt with "the nature, uses and manufacture of Ferro-Silicon with special reference to possible danger arising from its transport and storage." The investigation was placed in the hands of Dr. Copeman, with whom Mr. S. R. Bennett, one of H.M. Inspectors of Factories, and myself subsequently collaborated.

In my own Report, dealing specially with the chemical aspects of Ferro-Silicon, it was shown that certain grades of this ferro-alloy, notably those containing 35-60 per cent. of silicon, contained in most instances a considerable proportion of poisonous impurities and were liable to evolve poisonous gases when exposed to the action of moist air. The worst sample was shown to evolve 16.4 cubic feet of phosphoretted hydrogen per ton. These grades further showed a remarkable general tendency to disintegrate or fall to powder spontaneously, thus offering a still larger surface to the action of moisture.

On the other hand ferro-silicons containing 70-96 per cent. of silicon, although not free from poisonous impurities, did not show this tendency to disintegrate and hence were evidently safer as regards transport and storage. A third class, viz., those alloys containing from 10 to 30 per cent. of silicon were found to be practically free from poisonous impurities and showed an absence of this peculiar property of spontaneous disintegration.

About 70 samples of ferro-silicon were examined in 1909, and all but the last-mentioned class were manufactured in electric furnaces and were, almost without exception, of foreign origin.

As a result of the whole enquiry, regulations as to transport and storage of ferro-silicon were drafted by Dr. Copeman and finally adopted by the Board of Trade.

In 1910 Dr. Copeman suggested my examining a number of samples of Ferro-chromium with a view to ascertaining whether this form of ferro-alloy might be considered safe or not, inasmuch as, from information received by him, it appeared that certain ferro-chromium alloys not only showed a tendency to evolve poisonous gases but also exhibited the phenomenon of spontaneous disintegration.

I examined some 25 samples of ferro-chromium, and in December, 1910, submitted an *interim* report on the results obtained.

As a general outcome of my investigations it was found that, in certain respects, the ferro-chromium alloys showed marked differences to the ferro-silicon alloys. Thus some samples were extremely hard and others were very brittle, and there were intermediate degrees of hardness; but this varying hardness seemed to have little or no relationship with the proportion of the main constituent

of the alloy (viz., the chromium which varied between 60 and 70 per cent.) but appeared in certain cases to have some sort of relation to the carbon percentage, the brittle samples usually, but not always, containing a higher percentage of carbon (this constituent varied between 1.7 and 10 per cent.).

Preliminary tests for poisonous impurities in these ferro-chromium samples showed that these were only contained in about one-third of the samples, but in no case was any very large volume of phosphoretted hydrogen evolved by the action of water. The worst sample only yielded 0.52 cubic foot per ton. On the other hand, the worst samples had already disintegrated and may therefore, originally, have evolved a much greater proportion of poisonous gases.

Hence, while the ferro-chromium samples could not be considered as equal in danger to the ferro-silicon alloys, there seemed to be some potential danger in connection with their transport and storage, and an expression of opinion as regards their relative safety could not, so far, be considered as final.

Early in 1911, after having sent in the above-mentioned *interim* report on ferro-chromium alloys, I communicated with Dr. Copeman in reference to certain passages in his Report on Ferro-Silicon (Cd. 4958, 1909, p. 109) relating to the spontaneous disintegration of certain 50 per cent. grades of ferro-silicon, in the course of which he mentions that Dr. Heroult, of the Soc. Electro-Metallurgique Française, and Mr. Olsen, of Christiania, both advanced the view that the presence of *aluminium* was in some way connected with this tendency to spontaneous disintegration. Mr. Bennett also expressed a similar opinion.

Of these, however, only Mr. Olsen's opinion seems to have been based on experimental work, and Mr. Olsen states that in the course of his researches he found that, when during manufacture aluminium is *purposely* added "at certain percentages" (not specified) "the ferro-silicon can scarcely be kept a few minutes without falling to pieces."

Dr. Copeman had also informed me, in February, 1911, that some analyses specially made for him by Mr. Brearley in Sheffield in December, 1910, showed that a large proportion of aluminium was present in certain samples of ferro-chromium which had both spontaneously disintegrated and also evolved poisonous gases, while it was absent in another sample, which was stable and apparently free from poisonous impurities. (*See later.*)

The idea occurred to me, in connection with the above statements, that possibly the aluminium referred to might be present in the form of phosphide, of which several varieties are known, and which, like the calcium phosphide present in some ferro-silicons, are decomposed by water with evolution of phosphoretted hydrogen.

Dr. Copeman suggested that I should make a few tentative experiments, which I accordingly did, and I sent in a brief memorandum relating to them in March, 1911.

It appeared from my experiments that aluminium was present, and probably in the form of phosphide, in some samples of ferro-silicon and also of ferro-chromium which contained poisonous

impurities, and was absent in others, which were more or less free from these impurities.

The experiments were comparatively few in number and only qualitative, but the apparently very small amount of aluminium present in a soluble form made me somewhat doubtful as to whether any definite solution of the problem was involved in the assumption of aluminium phosphide as the disintegrating impurity.

I was therefore glad, later on, to have the opportunity afforded me in July, 1911, of making a more extended investigation in this connection, on various samples of ferro-alloys including, in addition to ferro-silicon and ferro-chromium, silico-manganese and ferro-manganese. A single sample of electro-manganese was also received and examined.

I now beg to report on the results of my more extended investigations.

My original reason for suggesting that aluminium might be present in certain ferro-alloys in the form of phosphide, was based on the behaviour of samples to very dilute acetic acid, which is without action on metallic aluminium, but which would extract this metal if present as phosphide. As a matter of fact, I did obtain dilute acetic acid extracts containing aluminium as well as calcium, but on estimating quantitatively the amount of aluminium present, presumably as phosphide, in this new series of ferro-alloys, I found that the proportion of the metal in this form was too small to account, in any way satisfactorily, for the phenomenon of disintegration, being in three instances less than 0.02 per cent. (*see* samples of ferro-silicon, Nos. 19 and 20, and silico manganese, No. 15 (*b*) in Table, Appendix I). I therefore abandoned this point of view and estimated instead, in a large number of the various ferro-alloys, the *total aluminium* present, with the object of confirming or otherwise the views held by certain experts above referred to, and which seemed in a measure already strengthened by the results of the analyses of some special samples of ferro-chromium, made in Sheffield for Dr. Copeman, to which I have also referred.

The methods employed for the estimation of the aluminium in these ferro-alloys, which I have described in detail at the end of this Report (*see* Appendix II), were of necessity somewhat complicated and tedious, inasmuch as they involved (1) the fusion of the alloy with alkaline carbonate, or with a mixture of alkaline carbonate and potassium nitrate, in order to bring the various constituents into a soluble form; (2) the treatment of the fused mass with water or with mineral acids, or both; (3) the separation of silica, carbon, &c., by filtration; (4) the precipitation of iron and aluminium as hydrates in the filtrate after silica, &c.; (5) the solution of these hydrates in hydrochloric acid, and (6) the separation of the aluminium from the iron, the aluminium being finally weighed as phosphate or oxide.

Notwithstanding the apparent complexity of the processes, the method had the advantage of being perfectly accurate and reliable and also avoided any extraneous introduction of aluminium as an impurity in the re-agents used. (*See* Appendix II.)

In addition to the aluminium estimations, of which in nearly every case two and sometimes three were made, I made a number

of preliminary qualitative tests, such as I had employed in my previous investigation of ferro-silicon (Cd. 4958, 1909), *e.g.*, hardness or resistance to fracture, tests for the presence or absence of phosphoretted hydrogen, &c., and I further estimated in certain samples the actual volume of phosphoretted hydrogen evolved by a known weight and, in many instances, also the silicon and iron content of the samples.

I have set out all these results in the Table appended to this Report (*see* Appendix I) and have included, in a special column, all the analytical *data* available from the various works at which the ferro-alloys were used. It will be seen from these *data* that only in very few instances are the works' analyses in any way complete and that the estimation of aluminium has not, as a rule, been attempted.

I will now proceed to discuss the bearing of my results as set forth in this Table in connection with the various classes of ferro-alloys examined.

Ferro-Silicon Samples.

I selected six samples of ferro-silicon ranging from 27 per cent. to 73 per cent. silicon, the first-mentioned being a typically "good" sample as regards freedom from poisonous impurities, the others being more or less "bad" in the sense that they had evolved poisonous gases and in some cases had actually disintegrated.

Preliminary tests.—The results of these tests were such as might have been anticipated from my previous examination of 70 samples in 1909. As regards "hardness" or resistance to fracture No. XXIV containing 27 per cent. silicon is very refractory, No. XIX (42 per cent. Si) is rather brittle and No. 2 (48 per cent. Si) rather more so, No. 20 (50 per cent. Si) is rather hard while No. 19 (52 per cent. Si) is a coarse powder, the result of spontaneous disintegration. No. 1 (a) (73 per cent. Si) is brittle and with this sample there was a coarse powder No. 1 (b) containing somewhat less silicon and said to be the result of its spontaneous disintegration.

As regards the qualitative test for poisonous gases all the samples (with the exception of No. XXIV), showed a more or less immediate blackening of silver nitrate paper on moistening with water, lead acetate paper being unaffected, thus demonstrating the presence of phosphoretted hydrogen. Some of the samples gave a powerful odour of this gas on crushing; No. XIX which yielded 16·4 cubic feet per ton of phosphoretted hydrogen when tested in 1909, still yields a powerful odour on crushing. (1912.) Nos. 19 and 20 when recently examined, yielded 3·8 and 0·8 cubic feet per ton respectively. On the other hand, No. XXIV gave only the faintest possible discolouration of nitrate of silver paper and a negative result on attempting to estimate the volume of phosphoretted hydrogen evolved.

Estimations of Aluminium.—It is interesting to note the results of the aluminium estimations in these samples. No. XXIV (27 per cent. Si) practically free from all poisonous impurities, was found to contain 0·5 per cent., while No. 1 (a) (73 per cent. Si) which evolved poisonous impurities showed 0·6 per cent., and 1 (b) the result of the

spontaneous disintegration of 1 (*a*) contained as much as 4·5 per cent., but No. 19 (52 per cent. Si) which is also the result of spontaneous disintegration, shows 1·1 per cent. of aluminium. No. XIX (42 per cent. Si) which is the worst sample as regards phosphoretted hydrogen, but which had not disintegrated, contains also rather more than 1 per cent. No. 2 (48 per cent. Si) also contains rather more than 1 per cent. Finally, No. 20 (50 per cent. Si) which is of English manufacture and rather harder than the rest, but not free from poisonous gases, contains 0·77 per cent.

Source of the aluminium found in the Samples.—The aluminium has in none of the above samples been added purposely (as in Mr. Olsen's experiments previously referred to) but is present as an impurity and its source is, without doubt, to be found mainly in the Anthracite coal used for the reduction of the Quartz (Si O_2) to Silicon (Si) as the following considerations will show :—

The Anthracite coal employed, contains as much as 10 per cent. of ash and sometimes more and this ash usually contains from 35 to 40 per cent. of alumina (Al_2O_3). Taking this percentage at about one-third of the weight of the ash this would correspond approximately to one-sixth by weight of aluminium (since alumina contains just over 52 per cent. of the metal) or one-sixtieth of the weight of coal used.

In a typical instance of the calculation of a "charge" used in the manufacture of ferro-silicon in the electric furnace, Dr. Copeman says on p. 66 of his Report (Supplement to 38th Annual Report of Medical Officer of the Local Government Board, 1909) :—

"Taking these different factors into consideration, the respective weights of the several ingredients required to make a charge for the production of say a 50 per cent. ferro-silicon, will be as follows :—

Quartz	...	...	...	...	150 kgms.
Anthracite	...	...	...	...	72 "
Steel Turnings	...	...	...	...	55 "
					277 "

and the amount of alloy actually obtained from the above charge will be 110 kgms. of 50 per cent. ferro-silicon."

Applying the foregoing calculation as to aluminium in the ash of the coal used, 72 kgms. of Anthracite will contain one-sixtieth of its weight or 1·2 kgms. of aluminium, and assuming that this finds its way into the finished product, 110 kgms. of 50 per cent. ferro-silicon will contain 1·2 kgms. of aluminium or 1·09 per cent.

Similarly to obtain a 27 per cent. ferro-silicon, about half the amount of Anthracite would be required for the reduction of the Quartz (Si O_2) and consequently, instead of 1 per cent. aluminium we should expect 0·5 per cent.

These calculated figures agree fairly closely with the percentages of aluminium which I have found in the various samples examined with the exception of 1 (*b*) which contained 4·5 per cent.

The main source of the aluminium is thus accounted for but even the Quartz used is said at times to contain alumina and may be a subsidiary source of this metallic impurity in the finished product.

Summary and Conclusions.—I had expected to find more marked differences in the percentages of aluminium in the samples of ferro-silicon examined, and I cannot therefore, without further detailed investigation, confidently conclude that the aluminium can be definitely regarded as the cause of this tendency to spontaneous disintegration of certain ferro-silicon alloys; yet many considerations occur to me as forcibly suggesting this conclusion, which I will briefly put forward.

In the first place the experiments of Mr. Olsen showing that purposely added aluminium causes sudden and rapid disintegration of certain ferro-silicon alloys, indicate that an excess of the metal over and above that present in the alloy as an impurity, accelerates the tendency to crumble.

Secondly, aluminium like carbon, is a powerful reducing agent, and its presence in the electric furnace may bring about a greater amount of reduction of calcium phosphate to calcium phosphide, and it is conceivable that much of the aluminium originally reduced from alumina might be re-oxidised and not appear in the finished product at all.

It is true that the percentage of aluminium found (mostly 1 per cent. except 1 (*b*) which contained 4.5 per cent.) seems small, but the question arises:—if it were possible to produce a 50 per cent. ferro-silicon avoiding the introduction of alumina in the process, would the product be more stable or, in other words, would it cease to disintegrate and, further, contain few or no poisonous impurities?

The attempt to produce such an aluminium-free ferro-silicon would be an interesting experiment as an extreme instance in contrast to Olsen's addition of aluminium. But, although no doubt possible in the laboratory, it is not easy from a practical point of view to see how aluminium could be entirely avoided as an impurity. Possibly, charcoal, which is free from alumina, might be used instead of anthracite coal.

I am the more inclined to put forward the above considerations since in the ferro-chromium alloys, which I will next proceed to discuss, the presence of aluminium does undoubtedly seem to have a disintegrating effect when in excess. It will further be noted that the possibility of excess of aluminium in ferro-chromium alloys is even greater than in ferro-silicon, because not only the coal used, but the chrome iron ore itself is liable to contain a considerable quantity of alumina. Another possible source of aluminium is the Thermite process referred to in Mr. Bennett's Report (p. 11). From these considerations it might be argued that the effect produced by aluminium in ferro-chromium alloys, might also obtain in ferro-silicon alloys, although so far the conclusion is not at present quite so obvious.

There is an older theory with reference to the spontaneous disintegration of ferro-silicon, viz., that 33 per cent., 50 per cent. and

69 per cent. ferro-silicons correspond to definite silicides of iron of a crystalline nature. This theory is discussed by Dr. Copeman in his Report (Cd. 4958, 1909, p. 110), but it does not appear to tally with other facts observed in connection with the occurrence of spontaneous disintegration in ferro-silicon samples and is in many respects unsatisfactory as an explanation of this very curious phenomenon.

Ferro-Chromium Samples.

As already noted in my introductory remarks, the majority of the samples of ferro-chromium which I examined and reported on in 1910 (25 in all) showed few or no poisonous impurities, but about one-third yielded a small proportion of poisonous gases; and some of them had actually disintegrated so that it was not possible to assert that all ferro-chromium samples were devoid of danger in connection with transport and storage. I have examined, for the purposes of this present report, some 15 samples. Some of these were very hard and some were very brittle; and here again, as noted in connection with the previous samples examined in 1910, there seems to be no definite relationship between the proportions of the main constituents (chromium and carbon) and the hardness of the samples as will be seen from the Table appended. (Appendix I.)

On testing for poisonous impurities, seven of the samples (Nos. 5 to 11 inclusive) were found practically free from them, two (Nos. 12 and 13) showed a partial tendency to disintegrate and the disintegrated portions contained poisonous impurities. Of these two, No. 13 (*a*) was so hard that it could not be crushed in an iron mortar while No. 12 was brittle (*see* Table).

I estimated the aluminium contained in No. 6 a typical "good" sample and found only 0.08 per cent.

Mr. S. R. Bennett who had, since 1909, assisted Dr. Copeman in collecting samples of the various ferro-alloys used in Sheffield and had contributed a report on the "composition and structure of ferro-silicon" to the general report issued by the Local Government Board on ferro-silicon already referred to (Cd. 4958, 1909), was not able to obtain for me any "bad" samples of ferro-chromium in Sheffield this last year (1911-12) so that I estimated the aluminium in two of the "bad" samples (Nos. 22 and 23 in Table) which I had received in 1910. The history of these samples was known and one had already been specially analysed for Dr. Copeman in December, 1910, by Mr. Brearley, of Sheffield. Both samples were known to have disintegrated and to have evolved poisonous gases. Taking No. 22 first, 22 (*a*) was in the form of rather hard lumps which on crushing and moistening with water showed the presence of phosphoretted hydrogen, but the actual volume obtained from a known weight was only equivalent to 0.26 cubic foot per ton. I found on estimating the aluminium, 1.1 per cent. of the metal.

22 (*b*) and 22 (*c*) were respectively small brittle lumps and coarse powder, both being the result of spontaneous disintegration of 22 (*a*).

22 (b) gave a marked qualitative re-action for phosphoretted hydrogen on crushing and moistening with water and yielded a rather larger volume of gas, equivalent to 0.52 cubic foot per ton. I found it contained 1.4 per cent. of aluminium.

22 (c) also showed a marked re-action for phosphoretted hydrogen, but as might be expected owing to its age and powdery condition yielded a smaller volume, equivalent to only 0.06 cubic foot per ton, but contained, like 22 (b), 1.4 per cent. of aluminium. (a) and (c) showed traces of sulphuretted hydrogen which is quite exceptional among ferro-alloys.

A more striking instance of marked difference in aluminium content was shown by sample No. 23 (see Table).

The history of this sample of ferro-chromium (No. 23) was briefly as follows:—44 casks of the alloy which had been manufactured in France in an electric furnace, were delivered to the user early in 1910. On sampling the casks on their arrival, it was found that in some of them the alloy consisted of "good clean lumps" varying somewhat in hardness; these are referred to as (1) "hard" and (2) "soft." In other casks the larger pieces were buried in a very fine powder and there could be distinguished two kinds of alloy described as (3) "friable lumps which broke to pieces when dropped on the floor," referred to as a "coarse" material; and (4) "friable pieces which broke when handled and could be rubbed to powder between the fingers" referred to as "fine." An analysis of these four kinds of material was made by Mr. Brearley with the result that he found in (1) and (2) no aluminium, in (3) 2.01 per cent. and in (4) 7.41 per cent. of aluminium.

I also analysed samples of the "hard" variety (1) and found 0.13 per cent. of aluminium and in No. (4) the "fine" variety 5.81 per cent.

In both the above instances (samples 22 (a) (b) and (c) and 23 (a) and (b)) the disintegrated portions of the alloys show a marked increase in the percentage of aluminium and the difference is especially striking in sample 23.

It is interesting to note that 23 (b), the "fine" material, still shows traces of phosphoretted hydrogen on moistening with water even after an interval of nearly two years. It is certain that this portion of the alloy must originally have evolved a large volume of poisonous gas.

Sources of aluminium present in samples of ferro-chromium.—The ferro-chromium samples examined show more marked contrasts as regards percentage of aluminium than the ferro-silicon samples, and also higher amounts. The reason for this lies doubtless in the fact that there are at least two main sources through which aluminium may be introduced into the alloy, viz., the coal used, which has been discussed under ferro-silicon and which contains about one-sixtieth of its weight of this metal, and the chrome iron-ore itself which is liable to contain as much as from 3 to 21 per cent. of alumina (Al_2O_3) or 1.5 to 10 per cent. of the metal. A possible third source is in the use of the Thermite process in which aluminium metal is used for the reduction of chromium ore (see Mr. Bennett's Report, p. 11).

Summary and Conclusions.—It is clear from the above detailed examination of various samples of ferro-chromium that the samples which are stable contain little or no aluminium while those which show a tendency to disintegrate contain an increased amount, and in some cases, a comparatively very high percentage of the metal. As regards the avoidance of this impurity in the manufacture of ferro-chromium, a still greater difficulty arises than with ferro-silicon owing to the occurrence of alumina in the chromium ore itself, apart from that present in the coal used. On the other hand it is equally clear from all that has been stated in the foregoing pages that while ferro-chromiums are not entirely free from danger, the dangerous samples have until recently, at any rate, been rather the exception than the rule.

Silico-Manganese Samples.

I had only two samples of this alloy sent me (see Table, Appendix I, Nos. 14 and 15). Neither sample was free from poisonous impurities and from the coarse powder which accompanied No. 15 and which was evidently the result of partial disintegration, I obtained a volume of phosphoretted hydrogen equivalent to nearly 0·4 cubic foot per ton. This is a greater quantity than I had obtained from any sample of ferro-chromium and, as in the case of these latter, obviously does not represent the total amount which must have been originally present.

There was a marked difference in the amount of aluminium found in the coarse powder as compared with the main bulk or "lump" of No. 15. The "lump" contained 0·2 per cent. while in the coarse powder 0·6 per cent. of aluminium was found. In No. 14 I found 0·7 per cent. of aluminium. This sample behaved somewhat anomalously; on powdering 200 grammes for analysis a considerable odour of phosphoretted hydrogen gas was noticeable. On testing other lumps I found them comparatively free from this impurity. Evidently the gas was occluded, in certain lumps, as although the odour was very marked on first crushing, only a comparatively slight reaction occurred on moistening the powder with water.

It would not be justifiable to draw any very definite conclusions from the quantity of aluminium found in these two samples. It is certainly interesting that in the coarse powder of No. 15 there is more aluminium than in the main bulk. The source of the aluminium in these alloys must be the coal used, as manganese ores contain little or no alumina.

The fact that the coarse powder of No. 15 appears to be the result of partial disintegration due to impurities, points to the possibility of worse products coming into the market.

Ferro-Manganese Samples.

I also received two samples of ferro-manganese (Nos. 16 and 17 in Table). They appeared not wholly free from poisonous impurities, but only showed traces. Whether these ferro-alloys are

likely to be dangerous can only be decided by further observation. Dr. Copeman, however, quotes two cases of spontaneous disintegration in connection with ferro-manganese, p. 7 of this report.

I found only 0.15 per cent. of aluminium in No. 16 which, as in the case of the silico-manganese alloys, is presumably derived from the coal used in reducing the oxides of iron and manganese; these latter would be practically free from alumina.

Electro-Manganese.

One sample of this interesting product, containing over 95 per cent. of manganese, was also sent to me by Mr. Bennett. It evolves hydrogen copiously in contact even with cold and still more with hot water, but no poisonous gases were found to be present. The only "danger" attaching to this product, which might possibly arise, would be the evolution of a considerable volume of hydrogen if water came into contact with a large bulk of it and hence the possible formation of an explosive mixture of air and hydrogen.

This suggestion of accident arising during transport or storage is not so improbable as might at first sight appear, since most people occupied in handling and using the material would be ignorant of the fact that it does decompose water at ordinary temperatures. It might therefore be important to caution users and others on this point.

H. WILSON HAKE.

APPENDIX I.

EXAMINATION OF VARIOUS FERRO-ALLOYS WITH SPECIAL REFERENCE TO ALUMINIUM CONTENT.

Identifying Number.	Nature of Alloy.	Date of Delivery to User.	Date of Collection of Sample.	Works' Analyses. (Percentages.)	Resistance to Fracture.	Qualitative Test for presence of Phosphoretted Hydrogen evolved by the action of water only.		Estimation of Phosphoretted Hydrogen. (Cubic Feet per Ton.)	Estimation of Aluminium in 100 parts of Ferro-Alloy.	Other Estimations (per cent.).	Remarks.
						(a) Discolouration of Silver Nitrate Paper.	(b) Discolouration of Lead Acetate Paper.				
XXIV	Ferro-Silicons.	— 1904	Mch., 1909	Si 27 Fe	Very refractory.	Very faint.	Nil	0.0	0.52 (a) 0.55 (b)	Si 27.5 27.1	(XXIV) Could only be powdered in an iron mortar. <i>Aluminium</i> estimated as <i>Al PO₄</i> in (a), and as <i>Al₂O₃</i> in (b).
XIX		— 1907	" "	Si 42 Fe	Rather brittle.	Immediate intense black.	Nil	16.4	1.04 (a) 1.24 (b)	Si 42.05	(XIX) Quite the worst sample as regards poisonous impurities out of 70 samples examined in 1909, but has not actually disintegrated. Still emits a powerful odour of phosphoretted hydrogen on crushing. <i>Aluminium</i> estimated as <i>Al PO₄</i> in (a) and as <i>Al₂O₃</i> in (b).
2		May, 1911	July, 1911	Si 48.04 Fe 47.8 Mn 1.01 Al 1.24 Ca nil. C 0.05 Mg trace	Brittle	Orange turning rapidly black.	Nil	—	1.24	—	(2) Distinct odour of phosphoretted hydrogen on crushing.
20		July, 1912	Jan., 1912	Si 50.99 Fe	Rather hard	Rapidly black.	Nil	0.8	0.77	Si 51.65 Fe 45.70	(20) English manufacture. Very slight odour on crushing. Gave .0019 per cent. <i>Aluminium</i> soluble in dilute acetic acid.
19		Nov., 1911	Nov., 1911	Si "52 per cent." Fe	Coarse friable powder.	Rapidly black.	Nil	3.8	1.11	Si 52.57	(19) Strong odour of phosphoretted hydrogen on crushing fine. Known to be the result of disintegration during transport. Gave .018 per cent. <i>Aluminium</i> soluble in dilute acetic acid.
1		June, 1911	July, 1911	Si 73.61 Fe 23.9 Mn 0.66 Al 0.6 Ca 0.57 C 0.15 S 0.06 P 0.03	(a) Brittle lumps. (b) Coarse powder.	Immediate intense black. Immediate intense black.	Nil	—	0.6	—	(1) Shows tendency to disintegrate, (b) intense odour of phosphoretted hydrogen on crushing fine.
5	Ferro-Chromiums.	July, 1911	July, 1911	Cr 66.0 Fe 24.6 C 7.89 Mn 0.16 Si 0.39 S 0.14 P 0.04	Brittle	Very faint.	Nil	—	—	—	Nos. 5-11 (ferro-chromium) are all practically free from poisonous impurities.
6		Mch., 1911	" "	Cr 66 C 8	Rather brittle.	Nil	Nil	0.0	0.08	—	
7		" "	" "	Cr 68.52 C 10.11	Rather hard	Very faint.	Nil	—	—	—	
8		May, 1909	" "	Cr 67.91 C 9.89	Very brittle.	Extremely faint.	Nil	—	—	—	
9		Mch., 1909	" "	Cr 72.39 C 6.6	Very hard	Extremely faint.	Nil	—	—	—	Nos. 12 and 13 (ferrochromium) show a tendency to disintegrate and the disintegrated portions contain poisonous impurities.
10		July, 1911	" "	Cr 64.1 C 6.95	Rather brittle.	Extremely faint.	Nil	—	—	—	
11		" "	" "	Cr 66.7 C 1.24	Excessively hard.	—	—	—	—	—	
12 ^a		June, 1911	" "	Cr 69.76 C 9.36	Very brittle. Coarse powder.	Nil.	Nil	—	—	—	
" ^b		" "	" "	—	Gradual dark brown.	—	—	—	—	—	22(b) consists of brittle lumps and 22(c) is a coarse powder, both known to be the result of the disintegration of 22(a).
13 ^a		" "	" "	Cr 66.30 C 0.94	Extremely hard. Coarse powder.	—	—	—	—	—	
" ^b		" "	" "	—	Gradual dark brown.	—	—	—	—	—	
22 ^a		May, 1910	May, 1910	Cr 67.9 C 8.5	Rather hard. Very brittle lumps. Coarse powder.	Gradual black. Rapidly black.	Slightly brown. Nil	0.26 0.52	1.13 1.08 1.39	—	
" ^b		" "	" "	—	—	Rapidly dark brown.	Slightly brown.	0.06	1.37	—	23(b). It is interesting to note that even now 23(b) shows a distinct but rather faint discolouration of silver nitrate paper after nearly 2 years.
23 ^a		— 1910	— 1910	Si 6.06 S .014 P .014 Al 0.0 Cr 67.56 Fe 18.37 C 8.2 Mn 0.55	Hard	—	—	—	0.13	—	
" ^b		— 1912	— 1912	Cr 58.8 Fe 19.5 C 6.95 Mn 0.32 Si 6.91 S .005 P .027 Al 7.41	Very fine powder.	Faint discolouration.	Nil	—	5.81	—	(14) This sample behaved rather anomalously; on powdering 200 grammes for analysis a powerful odour of phosphoretted hydrogen was observed. On testing other large lumps they did not show much poisonous impurity. Apparently this gas is occluded in some lumps and not in others.
14	Silico-Manganese.	July, 1911	July, 1911	Si 19.28 Fe 15.3 Mn 64.17 C 1.31 S .072 P .046	Very brittle.	Slight brown.	Nil	—	0.71 0.75	Si 18.29 18.62	
15 ^a		" "	" "	Si 23.98 Mn 69.63	Brittle	Gradually black.	Nil	—	0.18 0.19	Si 26.12 25.98	
" ^b		" "	" "	—	Coarse powder.	Immediate intense black.	Nil	0.39	0.62	Si 25.41 Fe 9.11	15(b). Apparently due to disintegration. Gave .011 per cent. <i>Aluminium</i> soluble in dilute acetic acid.
16	Ferro-Manganese.	July, 1911	July, 1911	Si 0.60 Fe 11.06 Mn 81.5 C 6.84	Brittle	Faint brown.	Nil	—	0.15	Si 1.02	(16) and (17). Ferro-Manganese—evidently not entirely free from poisonous impurities.
17		" "	" "	Mn 82.46	Brittle	Gradually brown.	Nil	—	—	—	
18	Electro-Manganese.	Aug., 1910	July, 1911	Mn 95.24	Rather hard.	Nil	Nil	—	—	—	(18). Electro-Manganese. This sample evolved hydrogen copiously in contact with water, but was free from poisonous impurities.

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APPENDIX II.

Methods of estimation of Aluminium, Silicon (and Iron) in samples of Ferro-Silicon.

(a) *Determination of Silicon.*—In all cases 1 gramme of the finely-powdered alloy from a typical sample, which had been ground and passed through a 60-inch sieve, was taken and fused either with potassium or sodium carbonate (Watson Gray, Journal of Iron and Steel Institute, 1901, No. II, p. 144). The quantity of carbonate used was about 4 grammes. An intimate mixture was made and transferred to a platinum crucible which was then heated, at first gently with a Bunsen burner and finally the temperature was raised to a bright red heat with a Méker burner, the crucible being covered with a lid. A somewhat vivid reaction occurs and the fused mass finally sinks to the bottom of the crucible in a state of quiescent fusion, indicating that the reaction is complete.

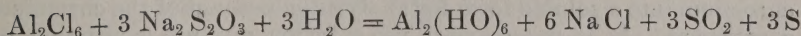
The crucible was allowed to cool and the fused mass extracted first with hot water and finally with hydrochloric acid, the solution being transferred to a porcelain dish. More hydrochloric acid was then added, using 15 cc. in all, and the contents of the dish raised to boiling while covered with a clock glass; 10 cc. of nitric acid are next added gradually, the cover washed and the whole solution containing some silica in suspension was evaporated to complete dryness on a water bath. The dry residue was then treated with a little hydrochloric acid, taken up in water, transferred to a beaker and after standing for some hours the deposited silica was filtered off, washed, dried, ignited and weighed and the silicon content of the sample thus determined.

(b) *Precipitation of iron and aluminium after removal of silica by filtration.*—The filtrate after silica contains all other constituents including iron and aluminium, and the next step consists in first precipitating these two constituents as hydrates and afterwards separating the usually small quantity of aluminium from the iron which is always present in large excess.

In the first place ammonium chloride is added, if necessary, to prevent the precipitation of manganese, &c., and then ammonia to the hot solution in slight excess and the solution is heated until it reacts only faintly alkaline.

The whole of the iron and aluminium present are thus precipitated as hydrates and free from all other constituents. The precipitate of the mixed hydrates is filtered and washed and next dissolved in hydrochloric acid. The solution in hydrochloric acid, now containing iron and aluminium only, is then treated as follows:—

- (1.) 2 grammes of sodium phosphate are added.
- (2.) Ammonia to slight turbidity which is cleared with not more than 2 cc. of hydrochloric acid.
- (3.) The solution is diluted to about 300 cc. with water and a solution of 10 grammes of sodium thiosulphate followed by 10 cc. glacial acetic acid diluted with an equal volume of water are next added, when the following reaction occurs—



The ferric chloride originally present is reduced to ferrous chloride and in the presence of sodium phosphate and acetic acid the aluminium is precipitated as aluminium phosphate, Al PO_4 .

The solution containing the sulphur and aluminium phosphate in suspension is next boiled for about 15 minutes to expel all the sulphur dioxide, the precipitate is allowed to settle, which it does almost immediately, and gradually transferred to a filter after washing with hot water by decantation, then further completely washed on the filter, dried, ignited and weighed. The sulphur is volatilised as sulphur dioxide during ignition, and phosphate of aluminium alone remains, and the determination is now complete.

The aluminium may be precipitated as hydrate instead of phosphate by omitting the addition of sodium phosphate in the first instance and partially neutralising the free acid before the addition of sodium thiosulphate, &c., but Brearley suggests the addition of phosphate since if phosphoric acid is originally present the aluminium is partly precipitated as phosphate and this leads to error. So far as the samples of ferro-silicon, which I examined, are concerned, however, I have tried both methods with practically identical results, showing that phosphoric acid if present at all can be only in minute traces (*see* samples XIX and XXIV).

The above method which is described in Fresenius' well-known handbook, is ascribed to Wöhler and is practically the only satisfactory method of separating aluminium from a large excess of iron.

It will be seen from the above that the process is lengthy and complicated but it is extremely accurate and reliable as the following facts show:—in the first place duplicate analyses were found to agree excellently, and the results of analyses which I made of some samples previously analysed at the Works independently, also agreed. I further tested the accuracy of the method by analysing a mixture of pure iron ammonium alum and potash alum in the proportion of two parts by weight of the former to one of the latter and containing therefore 7.74 per cent. of iron and 1.90 per cent. of aluminium with the result that the aluminium phosphate obtained corresponded to 2.07 per cent. aluminium. The very slight excess value was shown to be due to partial efflorescence of the alums.

Another special advantage of the method is the entire absence of aluminium as an impurity in the reagents used. I also tested this point by making a blank experiment, using two grammes of sodium phosphate and 10 grammes of sodium thiosulphate. I obtained an entirely negative result, that is to say, the precipitate obtained consisted wholly of sulphur which volatilised completely on ignition.

Method of estimation of Aluminium in samples of Ferro-Chromium.—So far as the aluminium is concerned this was determined exactly as described in the foregoing paragraphs but another method has to be adopted in order to bring the ferro-chromium into a soluble form for analysis on account of the chromium constituent. It is necessary to use a fusion mixture consisting of

three parts by weight of potassium or sodium carbonate with one part of potassium nitrate. One gramme of the finely-powdered alloy was taken from a typical sample (which had been ground and passed through a 60-inch sieve) and was mixed with about four times its weight of the fusion mixture, using a rather greater proportion if the chromium content was high. The fusion is best made in a nickel crucible as the reaction is rather vigorous and a platinum crucible is liable to be perforated. If the fusion is carefully conducted the chromium constituent is completely converted into chromate.

After completion of the reaction, which requires a high temperature, the fused mass may be completely removed from the crucible with hot water and is transferred to a porcelain dish. Potassium chlorate is next added to the aqueous solution which is then evaporated to a small bulk on the water-bath. At this stage the alkaline solution is carefully neutralised with hydrochloric acid, a very slight excess being added, and is then evaporated to dryness, more chlorate being added if necessary. The residue is taken up in water, filtered and in the filtrate the iron and aluminium are precipitated as hydrates with ammonia collected on a filter, washed and dissolved in hydrochloric acid. The aluminium may now be separated from the iron by the method fully detailed in the foregoing description of the analysis of ferro-silicon samples. Here, as before pointed out, the method is lengthy and somewhat complicated but is equally accurate as noted above.

Estimation of Silicon and Aluminium in samples of Silico-Manganese and Ferro-Manganese.—In the case of these two classes of ferro-alloys alkaline carbonates are used for fusion and the method is essentially the same as described under ferro-silicon.

Estimation of Iron in Ferro-Alloys.—In some cases the iron was estimated in the filtrate after the precipitation of aluminium either as phosphate or hydrate by methods which are all too well known to need special description.

Preliminary tests for Poisonous Gases and estimation of Phosphorated Hydrogen.—The methods and apparatus used in these tests were exactly as described in my Report on the Chemical Examination of Ferro-Silicon (Supplement to 38th Annual Report of the Medical Officer, Local Government Board, 1909, pp. 78 and 81).

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